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Crystallization studies of ZrO_2–SiO_2 composite gels

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Composite ZrO_2–SiO_2 powders were prepared using a gel route. Morphological and crystallographic features of ZrO_2 particles formed during the heat treatment, and the particle sizes of the composites have been investigated. The following polymorphic changes have been observed during the heat treatment: amorphous → metastable–cubic/tetragonal ZrO_2 → tetragonal ZrO_2 → monoclinic ZrO_2. SiO_2 crystallizes above 1273 K. The martensitic transformation of ZrO_2 (t → m) was observed *in situ*, when exposed to a high-energy electron beam. These results are important in the production of ZrO_2-toughened ceramics of controlled microstructure.

1. Introduction

Toughened ceramics have become important materials for high-temperature applications in recent years. Silica (SiO_2) and zirconia (ZrO_2) can be coprecipitated to form both glassy and crystalline phases of high toughness. The toughness of the ZrO_2–SiO_2 based ceramics is associated with the tetragonal–monoclinic transformation of ZrO_2 particles [1–3]. The stabilization of tetragonal phase up to very high temperatures appears possible by the control of microstructure using appropriate preparative and processing techniques [3, 4]. In recent years, the sol–gel technique has been widely adopted to produce ultrafine, high-purity single and multicomponent oxide glasses and ceramic composites [5]. Preparation of ZrO_2–SiO_2 composites by the alkoxide route has been reported in the literature [6]. We were interested in preparing ZrO_2–SiO_2 composites by the gel route using zirconyl nitrate and ethyl silicate as starting materials and in studying the phase stability and transformation of the resulting fine ZrO_2 particles in SiO_2. In this communication, we present our observations on the morphological and crystallographic features of the ZrO_2–SiO_2 composite gel powders. The present study is of importance in the preparation of ZrO_2-toughened ceramics.

2. Experimental procedure

The ZrO_2–SiO_2 composite gel powders of different compositions were prepared by dissolving zirconyl nitrate (purity 99.9%, which was made into a standard solution by dissolving in water) and ethyl silicate (commercial, Mettur Chemicals, India; estimated SiO_2 is about 40%). The solutions were mixed thoroughly by constant stirring. The mixing was done at 333 K and the hydrolysis was carried out by slow addition of aqueous ammonia solution. The precipitate was allowed to settle and the supernatant liquid was decanted after repeatedly washing with water. Completion of the precipitation was verified by the addition of alkali to the decanted portions of the solution, when no further precipitation occurred. The precipitate settled into a gel and it was dried slowly for several days (typically 1 w) under an infrared lamp. The initially dried gel was heated to 423 to 473 K for 3 d and the dried gel (agglomerate) was powdered in an agate mortar. The preparative schedule is shown schematically in Fig. 1. Five composite gel powders were thus prepared. The compositions were (ZrO_2/SiO_2), (0/100), (5/95), (25/75), (50/50) and (100/0) (mol %).

The gel powders were truly "composites" in the sense that the powders were a homogeneous mixture of very fine particles of ZrO_2 and SiO_2. The composite gel powders were dried until they were essentially free of organics. Powders were heat treated in a tube furnace. The temperatures used for heat treatment ranged from 673 to 1773 K. Samples were heated at a heating rate of $100\,K\,h^{-1}$ and held at the specified temperature for 2 h and then air quenched.

Powder characteristics were studied using powder X-ray diffraction on a powder X-ray diffractometer (Philips PW 1140). The morphology and structure were investigated using both an EM 301 transmission electron microscope (TEM 100 kV) and a Jeol 200 CX (200 kV) high resolution transmission electron microscope (HREM). Fine particles of the gel powders variously heat treated were held in holey carbon grids and particles with suitably thin cross-sections were scanned in the high-resolution studies. Powder surface areas were determined using nitrogen adsorption by the BET method on a Micromeritics, 2100E rapid surface area analyser. Infrared (IR) spectra were recorded (in KBr pellet) using a Perkin–Elmer 580 double beam IR spectrophotometer.

3. Results and discussion

The physical appearances of the powders are given in Table I, at various stages of heat treatment. Table I shows that the residual organics are present in the gel

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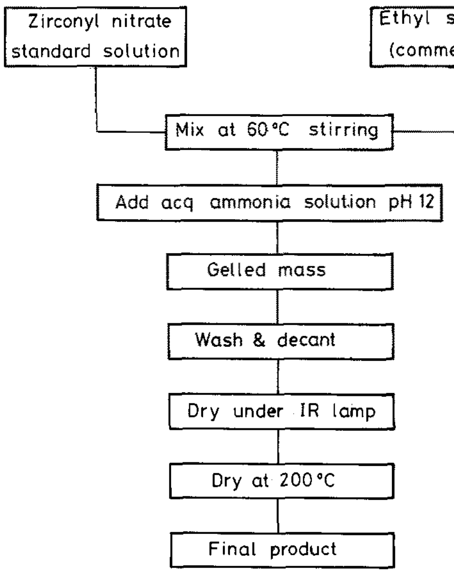

Figure 1 Schematic drawing of the preparative schedule.

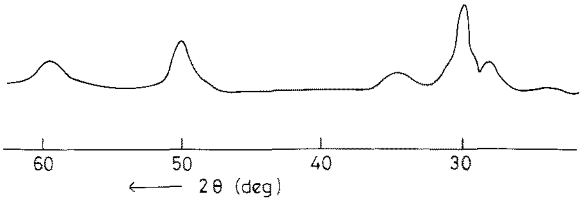

Figure 2 Powder X-ray diffractogram of typical C/T phase of ZrO_2 in the ZrO_2–SiO_2 composite.

powders up to about 873 K in the case of pure SiO_2 and ZrO_2–SiO_2 composites, whereas in the case of pure ZrO_2 the pure white colour appeared only at 1073 K after the elimination of residual organics.

The results of X-ray diffraction studies are summarized in Table II. The phases designated C/T give X-ray diffraction patterns from which it is often impossible to ascertain whether the patterns represent a cubic or tetragonal phase. One such pattern is shown in Fig. 2. Thus this is designated C/T, meaning a metastable–cubic/tetragonal phase. The presence of cubic phase of ZrO_2 in the composite has been supported by the IR spectra (Figs 3a to c). The observed IR absorption band frequencies are in good agreement with the values reported in the literature [7]. IR spectra of pure SiO_2 are also given for comparison. From Table II it can be seen that pure ZrO_2 heated up to 673 K (2 h) is in metastable–cubic/tetragonal form. The observed order of phase transformations is metastable–cubic/tetragonal → tetragonal → monoclinic and occurs as a function of increasing temperature.

That the initial phase of ZrO_2 formed in the gel-route preparations is cubic has been reported earlier by Yoldas [8]. Ultrafine powders of the as-prepared ZrO_2 were similarly reported to be cubic by Mazdiyasni [9]. However, Debsikdar [10] found that hydroxy preparations of ZrO_2 always resulted in the tetragonal phase and not the cubic phase. We feel that the observations are all essentially correct because the transformation of cubic to tetragonal phase involves just two simple and small strains [1] which are likely to be induced during the escape of gel-trapped water molecules. The volume difference is as small as 0.5% and the strains are approximately 1%. For the tiny crystallites of ZrO_2 (1 to 20 nm) involved in all these studies, the exact values of lattice parameters are blurred by the natural relaxation of a relatively large proportion of surface atoms. It should also be noted in this context that ZrO_2 is primarily an ionic material which allows fairly large surface atom relaxations. ZrO_2 prepared from the alkoxide route has been found to transform completely to the monoclinic form at 1073 K [10]. However, in the present case, the complete conversion of ZrO_2 to the monoclinic phase occurred at 1273 K (2 h). The presence of a small amount of tetragonal phase even at 1273 K is supported by the IR spectra of the sample (Fig. 5). Pure SiO_2 particles were found to crystallize when heated above 1273 K for 2 h (recognized through the strong X-ray reflection at $2\theta = 21.9°$ due to the cristobalite structure). The crystallization of SiO_2 appears to occur at a somewhat lower temperature in our studies as compared to the temperatures reported by Ono *et al.* [4]. Both the presence of tetragonal ZrO_2 crystallites in the composite and the mild exothermicity of the metastable–cubic to tetragonal transformation of ZrO_2 may reduce the crystallization temperature of amorphous SiO_2.

The "ZrO_2–SiO_2" composite gel as-prepared was amorphous to X-rays (Table II) and remained so even up to 1073 K. The temperature evolution of structure as revealed by X-ray diffraction is shown in Fig. 6, for the (25/75) composite. The (25/75) composite appears to crystallize into a metastable–cubic/tetragonal (C/T) form of ZrO_2 as the major phase, which persists up to 1473 K. Above this temperature C/T phase transforms into a tetragonal phase which is stable up to 1773 K. However, in the alkoxide-prepared ZrO_2–SiO_2 composites (40/60 wt % or (25/75)) Kamiya *et al.* [6] found that the structure of ZrO_2 was tetragonal up to 1273 K and that the crystallization of amorphous gel occurred at 823 K. The (50/50) composite is stable in the C/T form up to 1473 K but is transformed into a mixture of tetragonal and monoclinic (t + m) phases of ZrO_2

TABLE I Physical appearance of the gel powders

Composition ZrO_2–SiO_2 (mol %)	Temperature (K)						
	As-prepared	673	873	1073	1273	1473	1773
100– 0	DW	DW	LDW	PW	PW	PW	PW
50– 50	W	DW	LPW	PW	PW	PW	PW
25– 75	W	DW	LPW	PW	PW	PW	PW
5– 95	W	DW	LPW	PW	PW	PW	PW
0–100	W	DW	W	PW	PW	PW	PW

DW: Dirty White; LDW: Less Dirty White; LPW: Less Pure White; PW: Pure White; W: White.

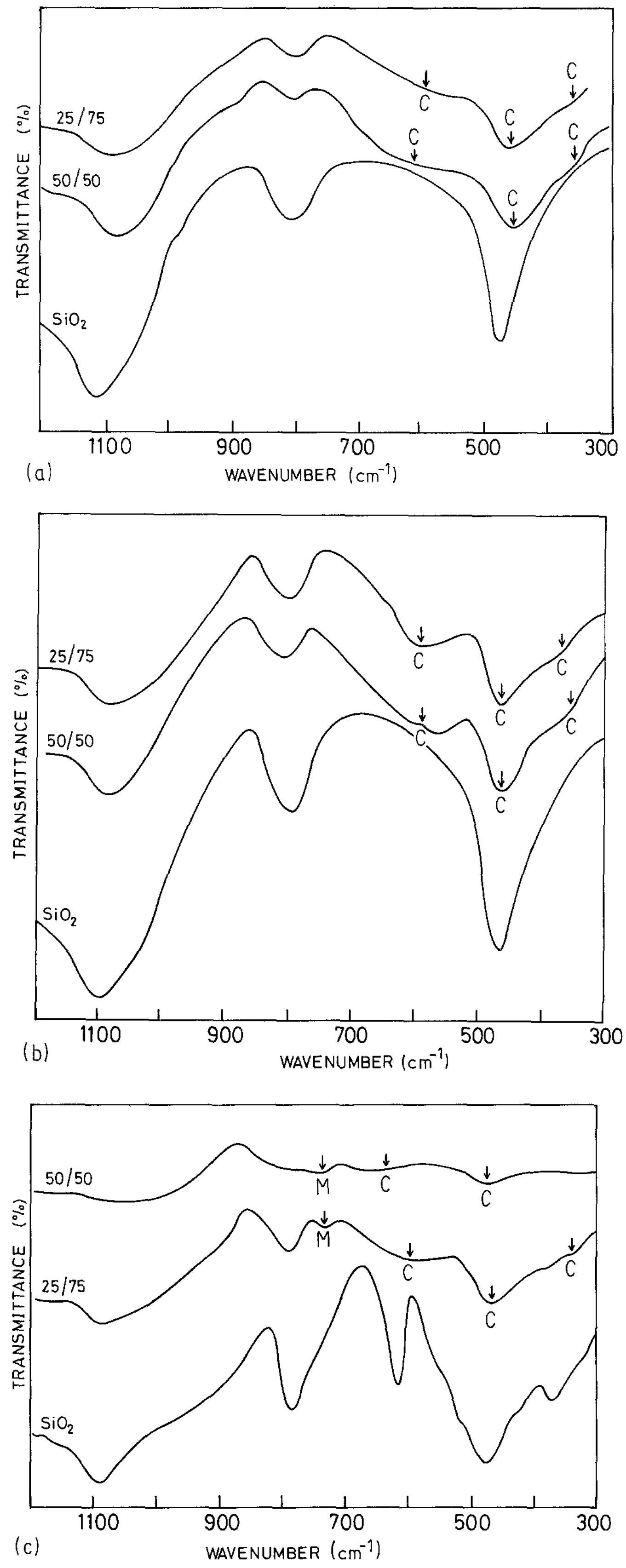

Figure 3 Infrared spectra for (25/75), (50/50) (ZrO_2/SiO_2) composites and pure SiO_2 heat treated at various temperatures. (a) 1273 K, (b) 1473 K, (c) 1773 K. M, monoclinic; T, tetragonal; C/T, metastable-cubic/tetragonal phases of ZrO_2.

at 1773 K. The (5/95) composite shows no major crystalline peaks of ZrO_2 even at 1273 K which may be attributed to the very low concentration of ZrO_2 in the "ZrO_2–SiO_2" composite as a result of which it is probably not detected in our X-ray diffraction studies.

The particle size and morphology as revealed in TEM studies may be summarized as follows. The electron micrographs (Fig. 7) of the (25/75) composite heat treated to 1773 K (2 h) appear to show ZrO_2 particles embedded in the SiO_2 matrix [11]. The particle sizes of the composite powders were extremely low; of the order of 50 nm in the case of (25/75) composite and 20 nm in the case of (50/50) composite. The particle shapes are almost invariably spherical. Particle sizes of pure, as-prepared ZrO_2 and SiO_2 could not be determined because they were all present as "powder agglomerates".

The results of the surface area analysis before high-

TABLE II Summary of XRD studies on the ZrO_2–SiO_2 composites*

ZrO_2–SiO_2 (mol %)	Temperature (K)						
	As-prepared	473	873	1073	1273	1473	1773
SiO_2					CR	CR	CR
0–100	A	A	A	A			
ZrO_2					–	–	–
SiO_2					CR	CR	CR
5–95	A	A	A	A			
ZrO_2					(C/T)	(C/T)	(C/T)
SiO_2					CR	CR	CR
25–75	A	A	A	A			
ZrO_2					C/T(M) 100%	C/T(M) 100%	T(M) 100%
SiO_2					CR	CR	CR
50–50	A	A	A	A			
ZrO_2					C/T(M) 100%	C/T(M) 100%	M(T) 74%
SiO_2		–	–	–	–	–	–
100–0	A	C/T	C/T(M)	M(T)	M(T)	M	M
ZrO_2		100%	63%	79%	89%	100%	100%

A: Amorphous; CR: Cristobalite; C/T: Cubic/Tetragonal; M: Monoclinic.

*The letter within the parenthesis indicate the minor phase. The percentages indicated are those of the major phase.

temperature treatment of the gel powders are shown in Fig. 8. While the surface areas are all generally high, the surface area for the (50/50) composite is significantly higher than the others.

The relative stability of cubic, tetragonal and monoclinic phases at high temperatures is influenced by two important factors; firstly the sizes of the ZrO_2 particles which are extremely small [12], and secondly the effect of SiO_2 present in the composite. Because of the smallness of crystallite size and the high temperatures, more open high-symmetry structures (which support high entropies) become stable. The cubic and tetragonal structures of ZrO_2, as pointed out earlier, possess nearly equal volume. When not present in a matrix, ZrO_2 particles are likely to stabilize in cubic form primarily due to their rather small sizes and hence

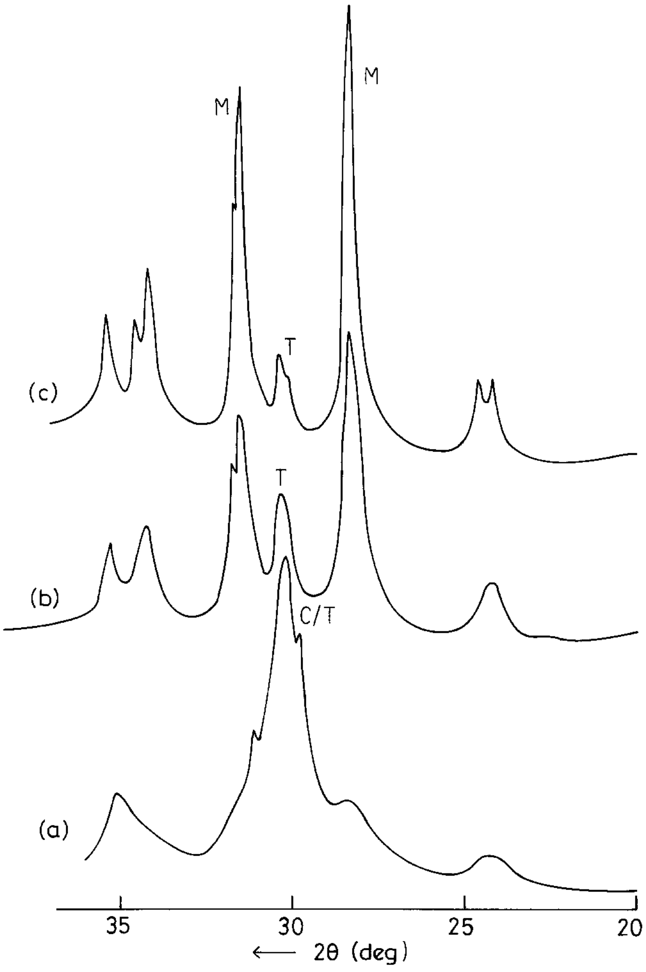

Figure 4 Powder X-ray diffractogram for pure ZrO_2 powder prepared by the zirconyl nitrate gel route and heat treated at various temperatures. (a) 673 K, (b) 1073 K, (c) 1273 K. M, monoclinic; T, tetragonal; C/T, metastable-cubic/tetragonal phase of ZrO_2.

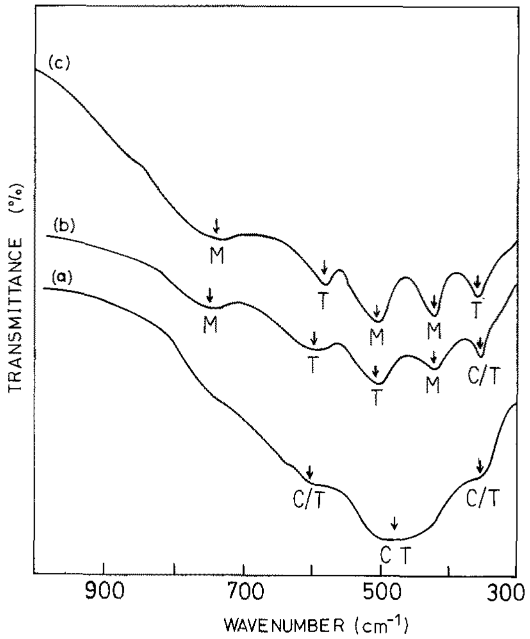

Figure 5 Infrared spectra for pure ZrO_2 powder heat treated at various temperatures. (a) As-prepared material; (b) 1073 K; (c) 1273 K. M, monoclinic; T, tetragonal; C/T, metastable-cubic/tetragonal phases of ZrO_2.

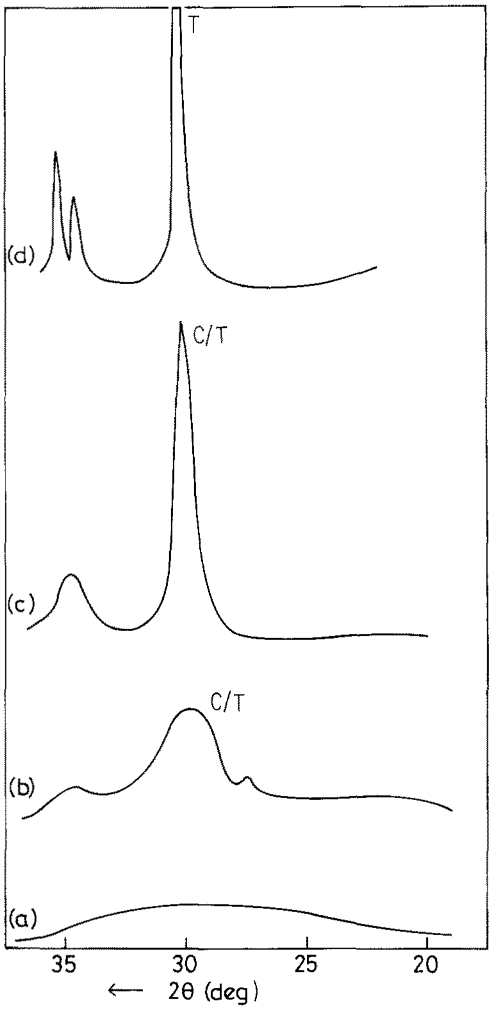

Figure 6 Powder X-ray diffractogram of typical (25/75) (ZrO_2/SiO_2) composite heat treated at various temperatures. (a) 1073 K; (b) 1273 K; (c) 1473 K; (d) 1773 K. M, monoclinic; T, tetragonal; C/T, metastable–cubic/tetragonal phases of ZrO_2.

large surface energies. The presence of SiO_2 in the matrix, however, appears to inhibit formation of the cubic phase and favour the tetragonal phase. This may again be partly due to interfacial energy which we suspect is low for SiO_2–t-ZrO_2 interfaces. However, we suspect that another subtle factor influences the formation of t-ZrO_2; that is the lower symmetry of SiO_2 crystallites which are in contact and which favour transformation to a similarly low symmetry (like-phases) tetragonal phase of ZrO_2.

Conversion of tetragonal to monoclinic phase is even more noticeably inhibited by the presence of SiO_2 in the composite. In many composite preparations the conditions are such that the ZrO_2 particles are either "coated" by SiO_2 or are embedded in a matrix of SiO_2. Because the t → m transformation involves a positive change of volume it is appealing to consider that the compressive stress due to the high-melting, low-expansivity, covalently bonded strong matrix of SiO_2 is not readily overcome by the low levels of expansion stress of small particles of t-ZrO_2 caused by the transformation volumes. Thus a critical size is required for the ZrO_2 particle (depending upon the composition and/or temperatures), so that the SiO_2 encasement is broken up due to stresses caused by the transformation volume. In the present instance, our preparative procedure does not preclude a "coating" of SiO_2 on ZrO_2 particles and this could perhaps be one of the reasons for the enhanced tetragonal regime of ZrO_2. A certain type of "blocking effect" of SiO_2 on the tetragonal to monoclinic transformation has been advocated by many workers [4, 6] in a similar spirit. A purely chemical origin of this effect cannot be ignored. The mutual solubility of ZrO_2 and SiO_2 is not clearly known. But a thin layer of $ZrSiO_4$ could form on the ZrO_2 particles which may be responsible for the inhibition of tetragonal to monoclinic (t → m) transformation. Our studies definitely indicate that absence of SiO_2 does lower the t → m transformation temperatures. Among all the composites, the (25/75) composite has shown the best stabilization effects of (C/T) and T phases of ZrO_2 which persists up to 1773 K. The (50/50) composite (67/33 wt % ZrO_2–SiO_2) showed the presence of t-ZrO_2 up to 1473 K.

Thus the concentration of two high-temperature structures namely (C/T), T and M of the fine ZrO_2 particulates in SiO_2 matrices are determined by a combination of physico-chemical factors. The percentage variation of (C/T) phases as a function of temperature in the case of pure ZrO_2 and (25/75) and (50/50) composites are shown in Fig. 9. The percentages were computed using the (X-ray scattering) peak intensity ratio method. Specifically $(1\,1\,1)_{c,t}$, $(1\,1\,1)_m$ and $(1\,1\,\bar{1})_m$ reflections were used in the calculations. The hatched region on the left-hand side for the three curves indicate the presence of amorphous phases at lower temperatures. In the case of pure ZrO_2 the transformation of (C/T) phases to monoclinic is gradual and reflects the distribution of particle sizes; the smaller particles tending to resist the transformation up to higher temperatures. During the coprecipitation, ZrO_2 is very likely to be evenly distributed in the SiO_2 matrix. SiO_2, being a covalently bonded material, establishes a semi-continuous phase during the hydrolysis of ethyl silicate. During the initial heat

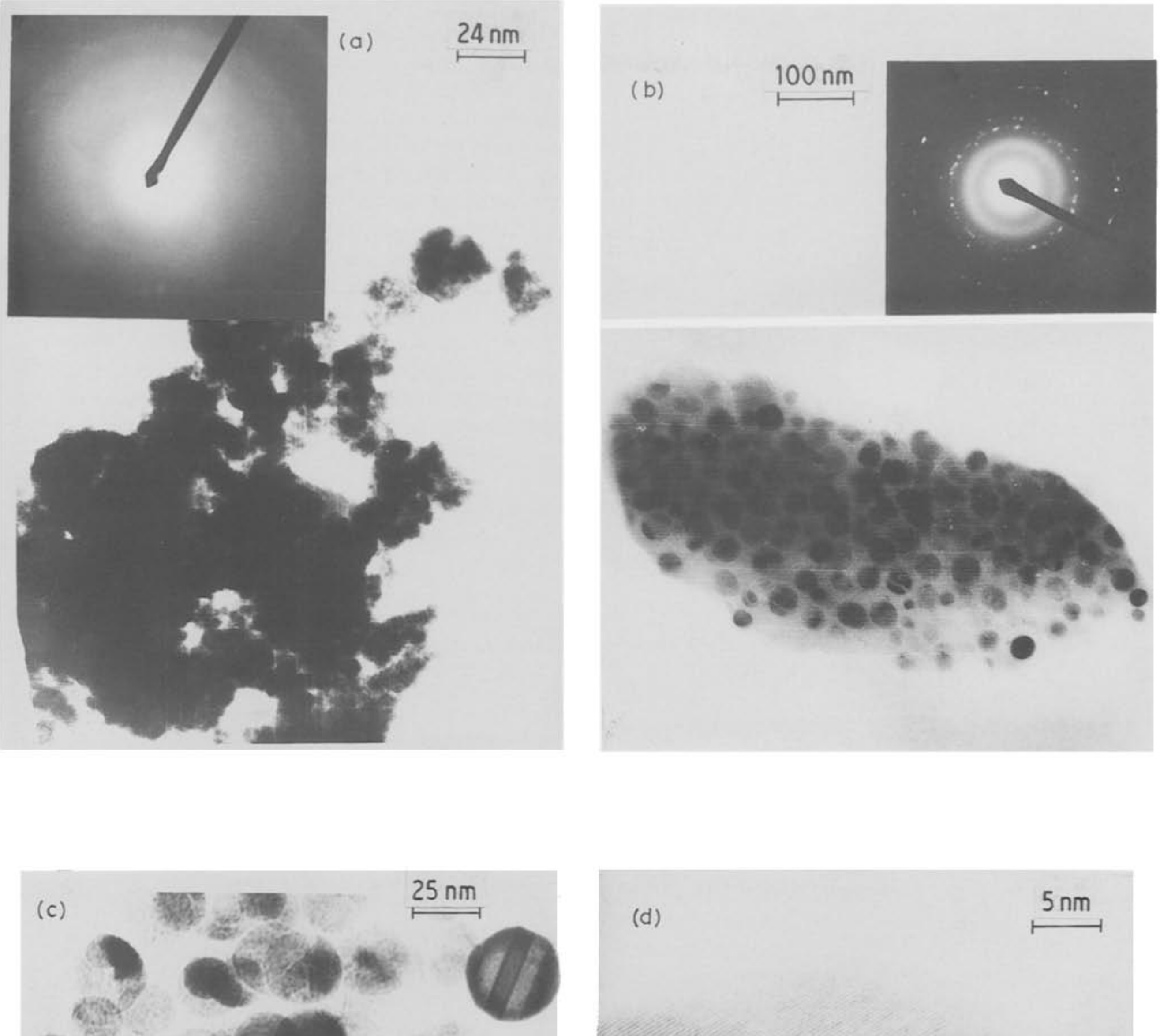

Figure 7 Transmission electron micrographs of typical (25/75) composite. (a) As-prepared powder agglomerate. Inset: electron diffraction pattern showing amorphous nature. (b) Powder heat treated to 1773 K. Inset: electron diffraction pattern showing polycrystalline t-ZrO_2. (c) Typical twinning observed on the constrained t-ZrO_2 particles after t → m transformation caused by impinging a high-intensity electron beam on the particle *in situ*. (d) High-resolution lattice image of a single twinned ZrO_2 particle (m-ZrO_2). Inset: electron diffraction pattern showing m-ZrO_2.

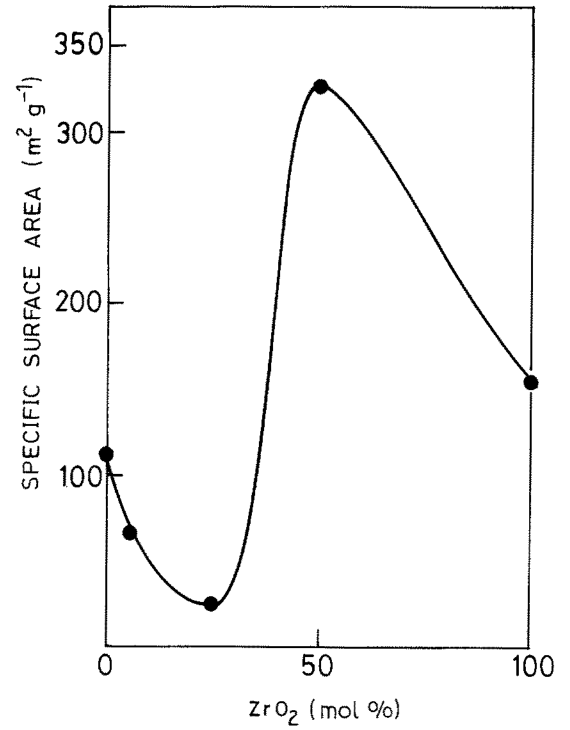

Figure 8 Specific surface area (m^2 g^{-1}) plotted against amount of ZrO_2 (mol %) in the ZrO_2–SiO_2 composite.

treatment, zirconium and oxygen ions migrate and form ZrO_2 particles as a hetero-phase. It is this feature which produces a distribution of inherently equisized (narrow distribution of particle sizes) tiny spherical particles of ZrO_2. Once these particles are formed from the featureless agglomerates they are already crystalline and are detected as a (C/T) phase. It is interesting to note from Table II, that the formation of (C/T) phases in both (25/75) and (50/50) composites is completed within a 200 K range (i.e. 1073 to 1273 K). The transformation of (C/T) phase into monoclinic in the case of (50/50) composite occurs gradually over about 300 to 400 K, which may be taken to indicate a fairly thick SiO_2 coating and a narrow distribution of small ZrO_2 particles.

The initial powder agglomerates are quite amorphous as typified by the 25/75 composite (Fig. 7a). Because the 25/75 composite is basically dilute with respect to ZrO_2, the fine spherical particles of t-ZrO_2 can be clearly identified only in heat-treated (up to 1773 K for 2 h) powders. While these particles are tetragonal as seen in the low-intensity beam in TEM (Fig. 7b) they become monoclinic when irradiated with an intense electron beam (which results in heating) in HREM. The typical twinning [1–3] that occurs during the transformation of the constrained tetragonal particles is quite evident from Fig. 7c. A more definitive lattice image of the twinned particle is provided in Fig. 7d.

The surface area measurements presented in Fig. 8 were performed on powdered agglomerates heat treated at 573 K. It is interesting to note that the highest surface areas (smallest particle sizes) are registered by the powders of (50/50) composite. While the origin of this observation is unclear to us, this is important from the point of view of choosing the processing schedules for high-temperature ZrO_2–SiO_2 composite preparations from gel routes.

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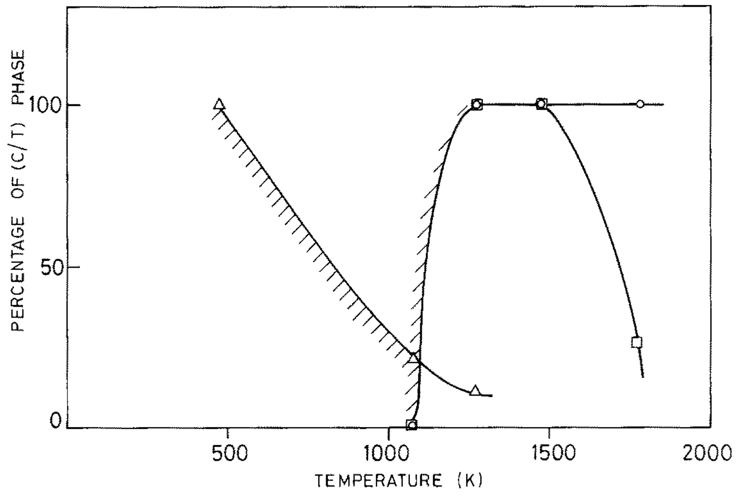

Figure 9 Percentage (C/T) phase of ZrO_2 plotted against temperature of heat treatment. The hatched region shows amorphous phases present. (△) Pure SiO_2, (○) 25/75, (□) 50/50.